

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

1,3,5,7,9,11,13,15-Octaazapenta-cyclo[9.5.1.1^{3,9}.0^{6,18}.0^{14,17}]octadecane-4,8,12,16-tetrone monohydrate: a methylene-bridged glycoluril dimer

 Pei-Hua Ma,^a Xin Xiao,^a Yun-Qian Zhang,^a Sai-Feng Xue^b and Zhu Tao^{b*}

^aKey Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, People's Republic of China, and ^bInstitute of Applied Chemistry, Guizhou University, Guiyang 550025, People's Republic of China.

Correspondence e-mail: sci.yqzhang@gzu.edu.cn

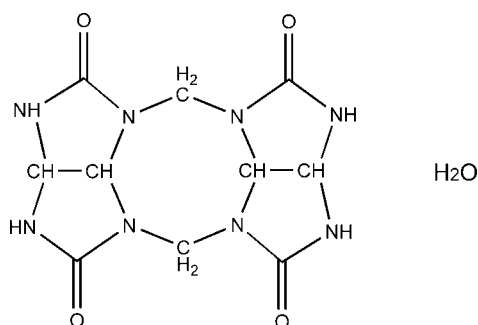
Received 23 July 2008; accepted 30 July 2008

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.033; wR factor = 0.089; data-to-parameter ratio = 10.4.

In the title compound, $\text{C}_{10}\text{H}_{12}\text{N}_8\text{O}_4 \cdot \text{H}_2\text{O}$, prepared from the reaction of glycoluril with paraformaldehyde, the organic molecule has *mm* symmetry. The asymmetric unit comprises one quarter of the molecule and a half-molecule of water. The dimer is formed by bridging two glycoluril molecules with methylene groups at the 1 and 6 positions. In the crystal structure, molecules are linked via $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, forming a two-dimensional framework.

Related literature

For general background, see: Zhao *et al.* (2004); Zheng *et al.* (2005).



Experimental

Crystal data

$\text{C}_{10}\text{H}_{12}\text{N}_8\text{O}_4 \cdot \text{H}_2\text{O}$	$V = 626.2$ (3) Å ³
$M_r = 326.29$	$Z = 2$
Orthorhombic, <i>Pmmm</i>	Mo $K\alpha$ radiation
$a = 10.292$ (3) Å	$\mu = 0.14$ mm ⁻¹
$b = 12.286$ (4) Å	$T = 298$ (2) K
$c = 4.9530$ (15) Å	$0.18 \times 0.13 \times 0.10$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	3977 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2005)	616 independent reflections
$T_{\min} = 0.975$, $T_{\max} = 0.986$	528 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	59 parameters
$wR(F^2) = 0.089$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{\max} = 0.18$ e Å ⁻³
616 reflections	$\Delta\rho_{\min} = -0.24$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1} \cdots \text{O1}^{\text{i}}$	0.86	2.01	2.8417 (17)	164
$\text{O1W}-\text{H1WA} \cdots \text{O1}^{\text{ii}}$	0.86	2.36	3.0241 (17)	135
$\text{O1W}-\text{H1WA} \cdots \text{O1}$	0.86	2.36	3.0241 (17)	135

 Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, -y + \frac{3}{2}, z$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *S SAINT* (Bruker, 2005); data reduction: *S SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We acknowledge the support of the National Natural Science Foundation of China (No. 20662003) and the Foundation of the Governor of Guizhou Province, China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2521).

References

- Bruker, (2005). *APEX2*, *S SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Zhao, Y. J., Xue, S. F., Zhu, Q. J., Tao, Z., Zhang, J. X., Wei, Z. B., Long, L. S., Hu, M. L., Xiao, H. P. & Day, A. I. (2004). *Chin. Sci. Bull.* **49**, 1111–1116.
- Zheng, L. M., Zhu, J. N., Zhang, Y. Q., Tao, Z., Xue, S. F., Zhu, Q. J., Wei, Z. B. & Long, L. S. (2005). *Chin. J. Inorg. Chem.* **21**, 1583–1588.

supporting information

Acta Cryst. (2008). E64, o1795 [doi:10.1107/S160053680802429X]

1,3,5,7,9,11,13,15-Octaazapentacyclo[9.5.1.1^{3,9}.0^{6,18}.0^{14,17}]octa-decane-4,8,12,16-tetrone monohydrate: a methylene-bridged glycoluril dimer

Pei-Hua Ma, Xin Xiao, Yun-Qian Zhang, Sai-Feng Xue and Zhu Tao

S1. Comment

In recent years, we have used different alkyl substituted glycolurils and glycoluril dimers as building blocks in the synthesis of partially alkyl substituted cucurbit[*n*]urils. In this work, we report the crystal structure of the title compound, a glycoluril dimer, Fig 1.

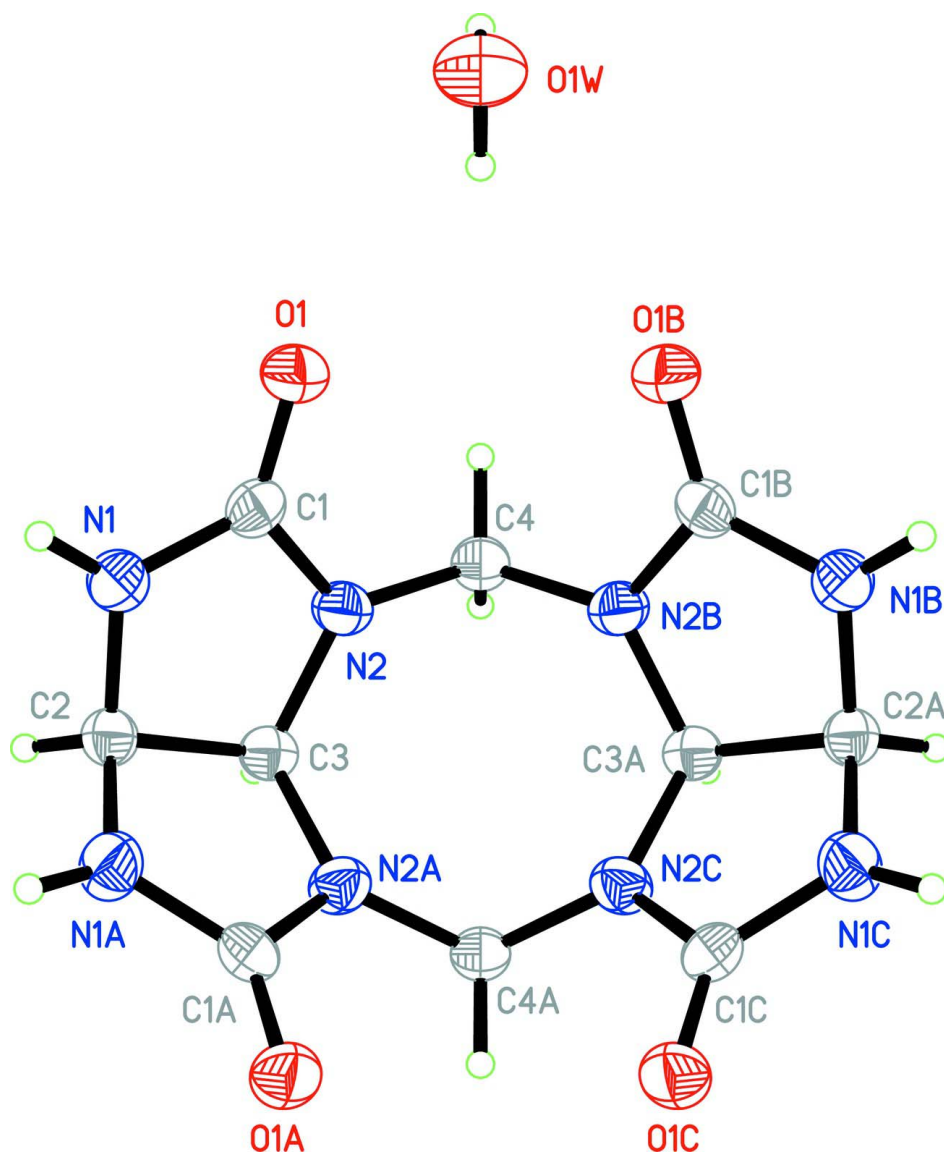
The molecule comprises two glycoluril units linked by methylene bridges at the 1 and 6 positions. Molecules have *mm* crystallographic symmetry and the asymmetric unit comprises one quarter of the molecule and a half molecule of water. In the crystal structure, molecules are linked *via* N1—H1⁺⋯O1⁻ and O1W—H1WA⁺⋯O1 hydrogen bonds forming a two-dimensional framework (Table 1 and Fig. 2).

S2. Experimental

A solution of glycoluril (7.0 g, 0.05 mol) in H₂SO₄ (50 ml, 25%) was added to a stirred solution of paraformaldehyde (6.0 g, 0.2 mol) in H₂SO₄ (150 ml) and the mixture was kept at 40°C for 5 h. Glycoluril (14.2 g, 0.1 mol) and H₂SO₄ (100 ml, 25%) were added in small proportions to this reaction mixture and the solution held at 80°C on a water bath for 5 h. After cooling to room temperature, the mixture was filtered to remove the insoluble residue and the filtrate was neutralized with aqueous NH₃ to pH 7. HCl (150 ml) was then added, the mixture, stirred for 10 min, then filtered again. The solid product was dissolved in 100 ml HCl, and then set aside for three weeks to form colourless crystals of I.

S3. Refinement

The water H atoms were located in a difference Fourier map and refined as riding on the O atom in these positions with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. All other H atoms were placed in calculated positions and refined as riding, with C—H = 0.97 Å (methylene) and 0.98 Å (methine), N—H = 0.86 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

**Figure 1**

The molecular structure of (I) showing the atom-labelling scheme (Symmetry codes: (A) $-x + 3/2, y, z$, (B) $x, -y + 3/2, z$, (C) $-x + 3/2, -y + 3/2, z$). Displacement ellipsoids are drawn at the 50% probability level.

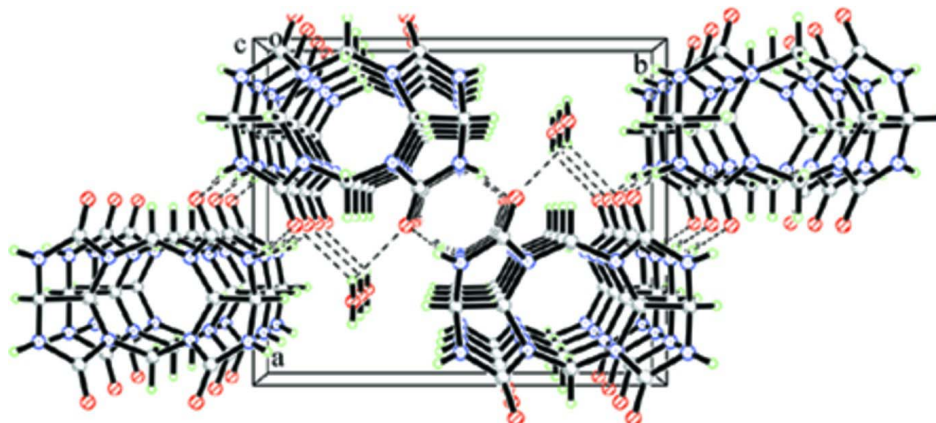


Figure 2

Packing diagram of (I). Hydrogen bonds are shown as dashed lines.

1,3,5,7,9,11,13,15-Octaazapentacyclo[9.5.1.1.3,9.0^{6,18}.0^{14,17}]octadecane-4,8,12,16-tetrone monohydrate

Crystal data

$C_{10}H_{12}N_8O_4 \cdot H_2O$

$M_r = 326.29$

Orthorhombic, *Pmmn*

Hall symbol: -P 2ab 2a

$a = 10.292$ (3) Å

$b = 12.286$ (4) Å

$c = 4.9530$ (15) Å

$V = 626.2$ (3) Å³

$Z = 2$

$F(000) = 340$

$D_x = 1.730$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 616 reflections

$\theta = 2.6$ – 25.1°

$\mu = 0.14$ mm⁻¹

$T = 298$ K

Prism, colorless

$0.18 \times 0.13 \times 0.10$ mm

Data collection

Bruker APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2005)

$T_{\min} = 0.975$, $T_{\max} = 0.986$

3977 measured reflections

616 independent reflections

528 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 25.1^\circ$, $\theta_{\min} = 2.6^\circ$

$h = -11 \rightarrow 12$

$k = -14 \rightarrow 14$

$l = -5 \rightarrow 5$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.089$

$S = 1.11$

616 reflections

59 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.1538P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.18$ e Å⁻³

$\Delta\rho_{\min} = -0.24$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1W	0.2500	0.7500	0.5795 (5)	0.0492 (7)
H1WA	0.3096	0.7500	0.4574	0.059*
C1	0.56573 (14)	0.59339 (12)	0.2017 (3)	0.0263 (4)
C2	0.7500	0.49067 (16)	0.0938 (4)	0.0272 (5)
H2	0.7500	0.4252	-0.0191	0.033*
C3	0.7500	0.59750 (16)	-0.0774 (4)	0.0254 (5)
H3	0.7500	0.5819	-0.2714	0.030*
C4	0.5795 (2)	0.7500	-0.1105 (4)	0.0265 (5)
H4A	0.5977	0.7500	-0.3027	0.032*
H4B	0.4859	0.7500	-0.0883	0.032*
N1	0.63278 (12)	0.50102 (10)	0.2503 (3)	0.0336 (4)
H1	0.6077	0.4527	0.3646	0.040*
N2	0.63117 (12)	0.65109 (9)	0.0058 (2)	0.0290 (4)
O1	0.46406 (10)	0.62196 (9)	0.3073 (2)	0.0341 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1W	0.0359 (14)	0.0614 (16)	0.0504 (16)	0.000	0.000	0.000
C1	0.0257 (8)	0.0270 (8)	0.0263 (9)	-0.0046 (6)	-0.0020 (6)	-0.0024 (6)
C2	0.0257 (11)	0.0248 (10)	0.0312 (12)	0.000	0.000	-0.0036 (9)
C3	0.0239 (11)	0.0281 (10)	0.0241 (11)	0.000	0.000	-0.0033 (9)
C4	0.0243 (11)	0.0290 (10)	0.0262 (11)	0.000	-0.0049 (8)	0.000
N1	0.0328 (8)	0.0307 (7)	0.0374 (8)	0.0027 (6)	0.0088 (6)	0.0078 (5)
N2	0.0245 (7)	0.0306 (7)	0.0319 (7)	0.0024 (5)	0.0038 (6)	0.0038 (5)
O1	0.0291 (6)	0.0352 (6)	0.0380 (7)	0.0024 (5)	0.0081 (5)	0.0019 (5)

Geometric parameters (\AA , $^\circ$)

O1W—H1WA	0.8616	C3—N2 ⁱ	1.4487 (16)
C1—O1	1.2214 (17)	C3—N2	1.4487 (16)
C1—N1	1.350 (2)	C3—H3	0.9800
C1—N2	1.3774 (19)	C4—N2 ⁱⁱ	1.4461 (16)
C2—N1 ⁱ	1.4395 (17)	C4—N2	1.4461 (16)
C2—N1	1.4395 (17)	C4—H4A	0.9700
C2—C3	1.563 (3)	C4—H4B	0.9700

C2—H2	0.9800	N1—H1	0.8600
O1—C1—N1	127.08 (14)	C2—C3—H3	111.6
O1—C1—N2	124.95 (14)	N2 ⁱⁱ —C4—N2	114.35 (17)
N1—C1—N2	107.97 (13)	N2 ⁱⁱ —C4—H4A	108.7
N1 ⁱ —C2—N1	113.86 (18)	N2—C4—H4A	108.7
N1 ⁱ —C2—C3	102.59 (11)	N2 ⁱⁱ —C4—H4B	108.7
N1—C2—C3	102.59 (11)	N2—C4—H4B	108.7
N1 ⁱ —C2—H2	112.3	H4A—C4—H4B	107.6
N1—C2—H2	112.3	C1—N1—C2	113.98 (14)
C3—C2—H2	112.3	C1—N1—H1	123.0
N2 ⁱ —C3—N2	115.16 (17)	C2—N1—H1	123.0
N2 ⁱ —C3—C2	103.14 (11)	C1—N2—C4	122.23 (14)
N2—C3—C2	103.14 (11)	C1—N2—C3	112.29 (13)
N2 ⁱ —C3—H3	111.6	C4—N2—C3	125.37 (15)
N2—C3—H3	111.6		
N1 ⁱ —C2—C3—N2 ⁱ	0.93 (16)	N1—C1—N2—C4	174.54 (13)
N1—C2—C3—N2 ⁱ	119.26 (13)	O1—C1—N2—C3	179.04 (14)
N1 ⁱ —C2—C3—N2	-119.26 (13)	N1—C1—N2—C3	-1.78 (18)
N1—C2—C3—N2	-0.93 (16)	N2 ⁱⁱ —C4—N2—C1	98.33 (19)
O1—C1—N1—C2	-179.74 (14)	N2 ⁱⁱ —C4—N2—C3	-85.8 (2)
N2—C1—N1—C2	1.10 (18)	N2 ⁱ —C3—N2—C1	-109.90 (16)
N1 ⁱ —C2—N1—C1	110.00 (16)	C2—C3—N2—C1	1.67 (17)
C3—C2—N1—C1	-0.06 (18)	N2 ⁱ —C3—N2—C4	73.9 (2)
O1—C1—N2—C4	-4.6 (2)	C2—C3—N2—C4	-174.51 (14)

Symmetry codes: (i) $-x+3/2, y, z$; (ii) $x, -y+3/2, z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O1 ⁱⁱⁱ	0.86	2.01	2.8417 (17)	164
O1 <i>W</i> —H1 <i>WA</i> \cdots O1 ⁱⁱ	0.86	2.36	3.0241 (17)	135
O1 <i>W</i> —H1 <i>WA</i> \cdots O1	0.86	2.36	3.0241 (17)	135

Symmetry codes: (ii) $x, -y+3/2, z$; (iii) $-x+1, -y+1, -z+1$.